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Copper-Mediated Nucleophilic Displacement Reactions of 1-Haloalkynes. Halogen–Halogen Exchange and Sulfonylation

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Some copper(I) and (II) compounds have been found to act as efficient reagents for the nucleophilic displacement of 1-haloalkynes. Copper(I) iodide smoothly transforms 1-bromoalkynes (**2**) into 1-iodoalkynes (**1**) which, on further treatment with copper(II) bis(arenesulfinate), are readily converted to the corresponding alkynyl aryl sulfones (**4**). The kinetic data of the halogen exchange between (4-chlorophenyl)ethynyl bromide (**2d**) and CuI have shown that the reaction is linearly dependent on the concentrations of both compounds. A mechanistic pathway involving the single electron transfer between 1-haloalkynes and copper(I) salt has been proposed for the present copper-assisted halogen exchange reaction at acetylenic carbon atom.

Due to the low affinity of *sp* carbon atom for Lewis bases, nucleophilic substitution is not so common a process for 1-haloalkynes[1,2] as is the case with haloalkanes or haloarenes. Low reactivity coupled with less easy access to acetylenic compounds have caused 1-haloalkynes to be rated low as a building block in organic synthesis. Classical methods for the preparation of 1-haloalkynes involve successive treatment of 1-alkynes with a strong base and a halogenating agent.[3] In these past two decades, however, several mild and more convenient preparative methods have become available,[4—10] which have considerably increased the potentiality of 1-haloalkynes as intermediates in organic syntheses. Representative haloalkyne-based organic syntheses include the palladium-catalyzed Stille-type coupling reaction for the preparation of asymmetric acetylenes,[11] enynes and enediynes,[12] and the copper-catalyzed Cadiot–Chodkiewicz reaction for the synthesis of asymmetric 1,3-diynes.[13,14] Such carbon–carbon bond forming reactions of 1-haloalkynes are usually carried out in the presence of some transition metal complex as catalyst or cocatalyst.[15]

1-Haloalkynes can also be used for the bond construction between an *sp* carbon and some heteroatoms other than halogen,[16] which includes the reactions with chalcogenide nucleophiles to obtain alkynyl ethers,[17] sulfides,[18—20] selenides,[18,21,22] and tellurides,[22] reactions with alkali metal amides[23] and hydrazides[24] to obtain *N*-alkynylated amines and hydrazines, reactions with phosphonate anions[25] or phosphite esters[26] to obtain *P*-alkynylphosphonates, and reactions with phosphines, phosphorodiamidothioites, and thiophosphate anions to yield alkynylphosphonium salts,[27] *P*-alkynylphosphonothioic diamides,[28] and *S*-alkynyl thiophosphates.[29] However, many other heteroatom nucleophiles either fail to react[30—32] or give unsatisfactory results due to low conversion[30,32] and/or concurrent side reactions such as addition, protonation, and oligomerization.[30,33]

In a manner analogous to the Cadiot–Chodkiewicz reaction, one may reasonably expect that the *sp* carbon–halogen bond in 1-haloalkynes can be activated in the presence of a copper salt, resulting in facilitated displacement of a halogen atom by a second heteroatom nucleophile. However, the literature to date contains very few such attempts as to copper or transition metals. The only successful example reported is the CuCl-assisted esterification of the *sp* carbon with *O*,*O*-dialkyl thiophosphate anion, where the use of an equimolar copper(I) salt is crucial.[29] In the absence of CuCl, the reaction does not take place.

In the present study, the scope and limitations of the copper-assisted nucleophilic displacement of 1-haloalkynes have been investigated for the Finkelstein-type halogen exchange at *sp*-carbon and the sulfonylation of 1-iodoalkynes with copper(II) bis(arenesulfinate)[34] as shown in Scheme 1, and the possible role of copper(I) or (II) as catalyst has been discussed briefly.

Results

Halogen–Halogen Exchange. We have examined the halogen–halogen exchange reaction of 1-haloalkynes **1a—3a** in the presence of an equimolar amount of copper(I) halide (CuI, CuBr, or CuCl) in acetonitrile at room temperature (Table 1, Entries 1—4,11,12). Interestingly enough, only the CuI-mediated conversion of bromide **2a** to iodide **1a** was feasible in acceptable yield under the conditions employed (Entry 3). Other combinations of acetylenic halides and copper(I) halides all failed to induce the halogen–halogen exchange. A similar observation has previously been made by Tanaka et al. in the Finkelstein-type halogen exchange of acetylenic halides,[30] where bromide **2a** was converted to chloride **3a** by treatment with excess tetraethylammonium chloride in hot dimethyl sulfoxide (DMSO). However, the reaction was very slow and accompanied by extensive hydro-

Table 1. Halogen-Halogen Exchange between Phenylethynyl Halides and Copper(I) Halides[a)]

$$\text{Ph–C}\equiv\text{C–X} \xrightarrow[\text{r.t., 24 h}]{\text{CuY}} \text{Ph–C}\equiv\text{C–Y} + \text{Ph–C}\equiv\text{C–C}\equiv\text{C–Ph}$$

1a : X = I
2a : X = Br
3a : X = Cl

5a

Entry	Substrate	CuY	Solvent	Product/%[b)]		Unchanged material/%[b)]
				Halide	Diyne **5a**	
1	**1a**	CuBr	MeCN	0	Trace	29
2	**1a**	CuCl	MeCN	0	Trace	Trace
3	**2a**	CuI	MeCN	**1a** 66	28	0
4	**2a**	CuCl	MeCN	0	3	7
5	**2a**	CuI	THF	**1a** 20	3	16
6	**2a**	CuI	Benzene	**1a** Trace	0	—[c)]
7	**2a**	CuI	CH_2Cl_2		No reaction	
8	**2a**	CuI	DMF	**1a** 43	18	0
9	**2a**	KI (1.0), CuBr (0.1)[e)]	DMF		No reaction	
10	**2a**	KI (1.0), CuBr (0.1)[d,e)]	MeCN	**1a** 70	17	Trace
11	**3a**	CuI	MeCN	0	Trace	2
12	**3a**	CuBr	MeCN	0	2	25

a) All reactions were carried out using a substrate (1.0 mmol) and copper salt (1.0 mmol) in the given solvent (5—10 mL) at room temperature for 24 h, unless otherwise stated. b) Isolated yield. c) Not determined. d) Reaction was extended to 96 h. e) Numerals in parentheses refer to molar equivalent.

$$\text{R–C}\equiv\text{C–X} \xrightarrow[-\text{X}^-]{\text{Y}^-,\ \text{Cu(I / II)}} \text{R–C}\equiv\text{C–Y}$$

1: X = I
2: X = Br
3: X = Cl

1: Y = I
4: Y = SO_2Ar

a: R = Ph
b: R = 4-MeC_6H_4
c: R = 4-$MeOC_6H_4$
d: R = 4-ClC_6H_4
e: R = 4-BrC_6H_4
f: R = 4-(MeOCO)C_6H_4
g: R = 4-NCC_6H_4
h: R = 4-$O_2NC_6H_4$
i: R = C_6H_{13}
j: R = 2,4,6-$Me_3C_6H_2$
k: R = 2-ClC_6H_4
l: R = 3-ClC_6H_4
m: R = 2-MeC_6H_4

4a-m: Ar = 4-MeC_6H_4
4n: R = Ar = Ph
4o: R = Ph, Ar = 1-naphtyl
4p: R = Ph, Ar = 4-$MeCONHC_6H_4$
4q: R = Ph, Ar = 4-$O_2NC_6H_4$
4r: R = Ar = 4-MeC_6H_4

Scheme 1.

dehalogenation to parent actylenic hydrocarbons, resulting in diminished yields of the products.

Among the solvents examined, acetonitrile gave the best results, probably due to the good solubility of CuI in this solvent. *N*,*N*-Dimethylformamide (DMF) also gave a homogeneous reaction mixture, but the yield of iodide **1a** was less satisfactory (Entry 8). In such solvents as benzene and dichloromethane, little or no exchange was observed (Entries 6,7), suggesting the importance of the solvating ability of organic solvent molecules toward a reactive copper species. When 1-haloalkynes were treated with potassium or ammonium halides (KI, KCl, Et_4NI, and Et_4NCl for **2a**; KBr and Et_4NBr for **1a**) under similar conditions in the absence of copper(I) salt, no halogen exchange was observed in acetonitrile. However, the addition of a catalytic amount of CuBr to a solution of **2a** and KI was found to induce slow formation of iodide **1a** (Entry 10).

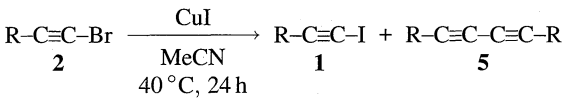
In the presence of CuI, a variety of 1-bromoalkynes **2a—i** have been converted to the corresponding 1-iodoalkynes **1a—i** in moderate to good yields (Table 2). In the case of aromatic alkynes **2a—c**, however, the coupling reaction leading to 1,4-diaryl-1,3-butadiyne **5a—c** occurred competitively. With aromatic substrates **2d—h** which bear an electron-withdrawing group on the ring, as well as aliphatic one **2i**, such coupling reaction did not take place (Entries 4—10).

The present unique one-way halogen–halogen exchange reaction opens a new route from aldehydes to 1-iodoalkynes **1**, since 1-bromoalkynes **2** are easily prepared by the dehydrobromination of 1,1-dibromoalkenes,[4,5)] which in turn are readily obtainable from the Wittig reaction of aldehydes and dibromomethylenetriphenylphosphorane. For the Stille-type C–C coupling reactions as well as sulfonyldehalogenation of 1-haloalkynes, 1-iodoalkynes are much preferred as substrate to 1-bromoalkynes.

Sulfonylation. Alkynyl sulfones are recognized as versatile intermediates in organic syntheses.[34,35)] The sulfonyl group can be used not only as the activator of the triple bond toward nucleophiles and dipolarophiles, but also as an easily removable protection unit for molecular framework modification. In spite of their synthetic utility and versatility, however, known routes to alkynyl sulfones are still limited in terms of convenience and generality.[34)]

Alkali metal sulfinates are commonly used as the nucleophilic sulfonylating agent for haloalkanes. We have recently reported that iodoarenes can also be smoothly sulfonylated

Table 2. Iodination of 1-Bromoalkynes **2a—i** with CuI[a]



Entry	Bromoalkyne	R	Iodoalkyne **1**/%[b]	1,3-Diyne **5**/%[b]
1	**2a**	C_6H_5	**1a** 69	**5a** 28
2	**2b**	4-MeC_6H_4	**1b** 26	**5b** 10
3	**2c**	4-$MeOC_6H_4$	**1c** 41	**5c** 11
4	**2d**	4-ClC_6H_4	**1d** 79	N.D.[d]
5	**2e**	4-BrC_6H_4	**1e** 54	N.D.[d]
6	**2f**	4-$MeO_2CC_6H_4$	**1f** 84	N.D.[d]
7	**2g**	4-NCC_6H_4	**1g** 40	N.D.[d]
8	**2g**[c]	4-NCC_6H_4	**1g** 59	N.D.[d]
9	**2h**	4-$O_2NC_6H_4$	**1h** 65	N.D.[d]
10	**2i**	C_6H_{13}	**1i** 37	N.D.[d]

a) All reactions were carried out by stirring a mixture of **2** (0.50 mmol), CuI (1.0 mmol), and acetonitrile (10 mL) at 40 °C for 24 h, unless otherwise noted. b) Isolated yield. c) Stirred in DMF (10 mL) for 10 min. d) Not detected.

by sulfinate anion in the presence of a copper salt.[36] When acetylenic iodide **1a** was treated with sodium 4-methylbenzenesulfinate, the expected alkynyl sulfone **4a** was obtained only in low yield, irrespective of solvents, reaction time, and agitation modes (Table 3, Entries 1, 2). Addition of a copper salt such as CuI, CuCN, $Cu(OAc)_2$, or $Cu(acac)_2$

Table 3. Sulfonylation of 1-Iodoalkyne **1a** with 4-Methylbenzenesulfinates The Effect of Reagent Types and Solvents on the Product Yields[a]

Entry	Reagent (equiv)[b]	Conditions			Yield/%[d]		
		Solvent	Method[c]	Time/h	**4a**	**5a**	Unchanged **1a**
1	TosNa (1.0)	DMF	M	24	11	0	57
2	TosNa (1.0)	THF	U	4	16	0	72
3	TosNa (1.2), CuI (1.0)	DMF	M	24	34	39	6
4	TosNa (1.2), CuI (0.1)	DMF	M	24	28	19	24
5	TosNa (1.2), CuCN (1.0)	DMF	M	24	25	25	3
6	TosNa (1.2), $Cu(OAc)_2$ (1.0)	DMF	M	24	28	32	15
7	TosNa (1.2), $Cu(acac)_2$ (1.0)	DMF	M	24	20	8	0
8	Tos_2Cu (0.6)	DMF	M	24	50	5	23
9	Tos_2Cu (0.6)	MeCN	M	24	50	0	24
10	Tos_2Cu (0.6)	H_2O	M then U	21 3	60	Trace	17
11	Tos_2Cu (0.6)	THF	U	8	69	0	10
12	Tos_2Cu (0.67)	THF	M	24	73	0	2
13	Tos_2Cu (0.67)	THF	U	4	77	Trace	Trace
14	TosH (1.34), Cu_2 carbonate (0.335)	THF	U	4	75	Trace	4
15	TosNa (1.34), $MeSO_3H$ (1.34), Cu_2 carbonate (0.335)	THF	U	4	74	Trace	11
16	TosNa (1.34), Cu_2 carbonate (0.335)	THF	U	4	27	Trace	46
17	Tos_2Cu (0.67)	AcOH	U	4	58	Trace	Trace
18	Tos_2Cu (1.0)	THF	U	3	64	0	Trace
19	Tos_2Cu (1.0)	CH_2Cl_2	U	7	63	0	Trace
20	Tos_2Cu (1.0)	EtOH	U	3	58	0	Trace
21	Tos_2Cu (1.0)	DMF	M	24	47	7	Trace
22	Tos_2Cu (1.0), TosNa (1.0)	THF	U	3	32	0	0

a) All reactions were carried out using **1a** (1.0 mmol) in the given solvent (3.0 mL). b) TosNa = sodium 4-methylbenzenesulfinate; Tos_2Cu = copper(II) bis(4-methylbenzenesulfinate); TosH = 4-methylbenzenesulfinic acid; Cu_2 carbonate = commercial basic copper carbonate of approximate composition $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$. c) Abbreviations M and U refer to magnetic stirring and ultrasonic irradiation, respectively. d) Isolated yield.

raised the yield of **4a**, but concurrent formation of 1,3-diyne **5a** became appreciable (Entries 3—7). After many attempts, the use of a slight excess of copper(II) bis(4-methylbenzenesulfinate) (0.67 equiv) in THF proved to be most efficient for converting **1a** to sulfone **4a** in good yield (Entry 13). This copper(II) salt can also be prepared in situ from a basic copper carbonate and 4-methylbenzenesulfinic acid (Entries 14, 15). The use of a lesser amount or much excess of copper sulfinate did not improve the yield (Entries 11, 18). As to the reaction medium, even water (Entry 10) and acetic acid (Entry 17) could be used, but THF gave the best results. Under heterogeneous conditions, the formation of diyne **5a** was mostly suppressed and the resulting inorganic copper compound was easily removed by filtration during workup. Ultrasonic irradiation could shorten the reaction time considerably (Entries 12, 13). Other transition metal complexes and salts such as $Ni(acac)_2$, $Fe(acac)_3$, $Co(acac)_2$, AgOAc, and $PdCl_2$ were all found to be ineffective as the catalyst for sulfonylation.

Using the present procedure, a variety of 1-alkynyl aryl sulfones **4a**,**f**—**j**,**n**—**r** were prepared from the corresponding 1-iodoalkynes; the results are listed in Table 4. The use of 1-bromo- or 1-chloroalkynes in place of 1-iodoalkynes led to the formation of a significant amount of unidentified by-products, reducing the yield as well as the purity of alkynyl sulfones **4** obtained (Entries 2, 3, 8).

Kinetic Study and Additive Effect. Little mechanistic information is available at present for the copper-mediated nucleophilic displacement reaction of 1-haloalkynes.[37] The present halogen–halogen exchange has been found to proceed under mild homogeneous conditions, so the kinetic study has been undertaken using (4-chlorophenyl)ethynyl bromide **2d** and CuI as reagents in acetonitrile at 40 °C.

In the presence of excess CuI, bromide **2d** was converted smoothly to iodide **1d** without accompanying side products. The disappearance of **2d** was found to obey the pseudo first-order kinetics (Fig. 1, Eq. 1):

$$v = -\mathrm{d}[\mathbf{2d}]/\mathrm{d}t = -k_0[\mathbf{2d}]. \quad (1)$$

With the increase of initial CuI concentration $[CuI]_0$ from 3.0 to 7.5×10^{-2} M (1 M = 1 mol dm^{-3}), good pseudo first-order kinetic profiles were always observed up to 50% conversion stage (Fig. 2), and the pseudo rate constants were directly proportional to the initial concentration $[CuI]_0$ (Eq. 2). Combining Eqs. 1 and 2, one can obtain the second order rate Eq. 3 :

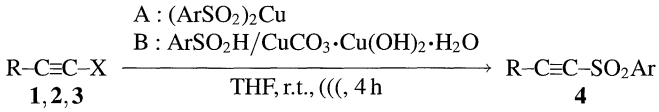
$$k' = 5.1 \times 10^{-4} \quad [CuI]_0 \quad (2)$$

$$k = -k[\mathbf{2d}][CuI] \quad (k = 5.1 \times 10^{-4}\ \mathrm{M^{-1}\,s^{-1}}) \quad (3)$$

Equation 3 tells us that one molecule each of bromide **2d** and CuI is involved at initial stage of the halogen exchange; this rules out possible involvement of multiple copper species at least up to 50% conversion. As the concentration of CuI approaches a stage of saturation, the experimental rate plot gradually deviated from the theoretical one (Fig. 3). This finding suggests that the overall reactivity of the substrate is reduced as the degree of aggregation of CuI molecules increases.

The effect of additives on the iodination of **2d** is shown in Table 5. 1,2-Dinitrobenzene (DNB), an established elec-

Table 4. Sonochemical Synthesis of 1-Alkynyl Sulfones 4[a]



Entry		Haloalkyne	Sulfinate		Sulfone	
			Ar	Reagent[b]		Yield/%[c]
1	**1a**	PhC≡Cl	4-MeC_6H_4	A	**4a**	77
2	**2a**	PhC≡CBr	4-MeC_6H_4	A		0[d]
3	**3a**	PhC≡CCl	4-MeC_6H_4	A		0[d]
4	**1f**	4-$MeO_2CC_6H_4C$≡Cl	4-MeC_6H_4	A	**4f**	64
5	**1g**	4-NCC_6H_4C≡Cl	4-MeC_6H_4	A	**4g**	40
6	**1h**	4-$O_2NC_6H_4C$≡Cl	4-MeC_6H_4	A	**4h**	6
7	**1i**	$C_6H_{13}C$≡Cl	4-MeC_6H_4	A	**4i**	34
8	**2i**	$C_6H_{13}C$≡CBr	4-MeC_6H_4	A	**4i**	14
9	**1j**	2,4,6-$Me_3C_6H_2C$≡Cl	4-MeC_6H_4	A	**4j**	56
10	**1a**	PhC≡Cl	Ph	B	**4n**	73
11	**1a**	PhC≡Cl	1-Naphtyl	B	**4o**	94
12	**1a**	PhC≡Cl	4-$MeCONHC_6H_4$	B	**4p**	66
13	**1a**	PhC≡Cl	4-$O_2NC_6H_4$	B	**4q**	50
14	**1b**	4-MeC_6H_4C≡Cl	4-MeC_6H_4	B	**4r**	49

a) All reactions were carried out using a mixture of haloalkyne (1.0 mmol), reagent A or B in THF (3.0 mL) at room temperature under sonication for 4 h. b) Reagents A: copper(II) bis(4-methylbenzenesulfinate) (0.67 mmol); B: 4-methylbenzenesulfinic acid (1.34 mmol)/$CuCO_3$·Cu-$(OH)_2$·H_2O (0.34 mmol). c) Isolated yield. d) A complex product mixture was obtained.

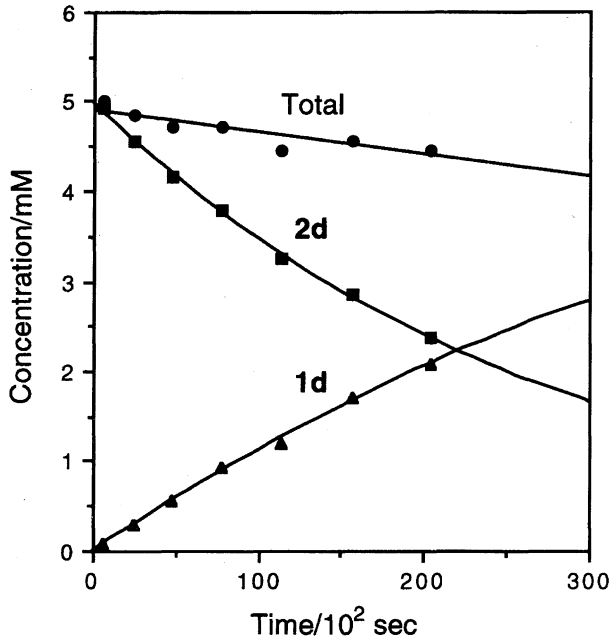


Fig. 1. Reaction profile for the iodination of **2d** (5.0×10^{-3} M) with CuI (7.5×10^{-2} M) in acetonitrile at 40 °C.

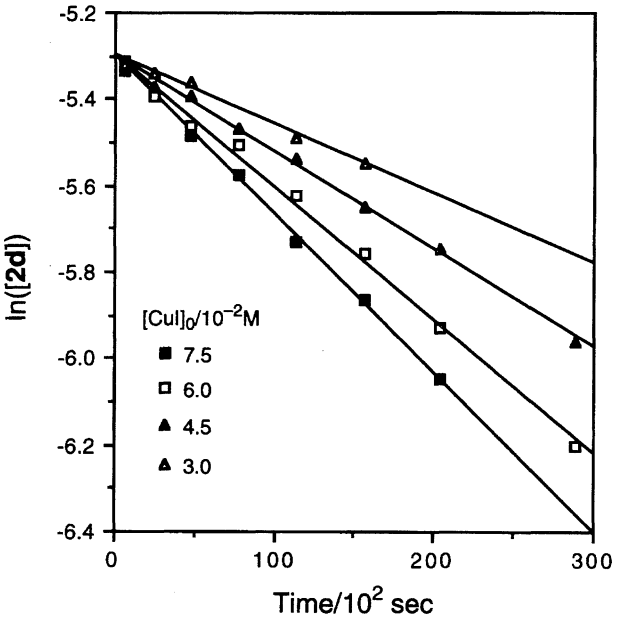


Fig. 2. Kinetic dependence on CuI concentration. $[\mathbf{2d}]_0 = 5.0\times10^{-3}$ M in acetonitrile at 40 °C.

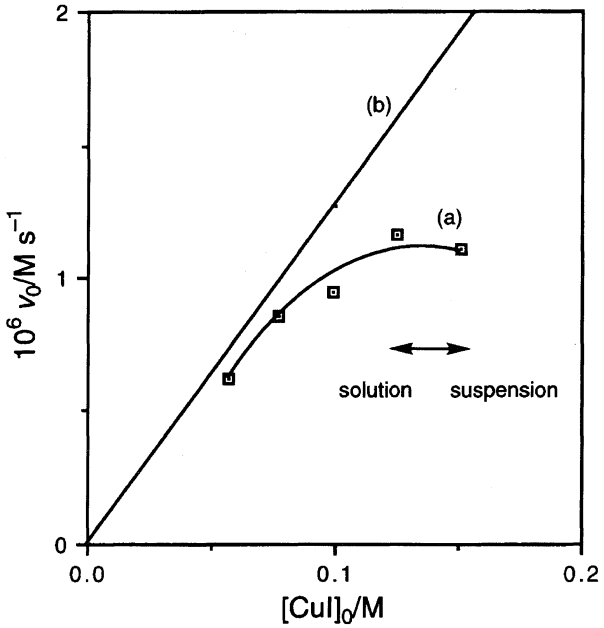


Fig. 3. (a) Kinetic plot under the conditions of near saturation of CuI. $[\mathbf{2d}]_0 = 2.5\times10^{-2}$ M, in acetonitrile at 40 °C. (b) Theoretical plot according to Eq. 3.

Table 5. The Effect of Additives on the Iodination of **2d** with CuI[a)]

Entry	Additive	Yield of **1d**/%[b)]
1	None	79
2	$1,2\text{-}(NO_2)_2C_6H_4$ (5.0 equiv)	83[c)]
3	$Ph_2C{=}CH_2$ (5.0 equiv)	24[d)]
4	2,6-*t*-Bu(4-Me)C_6H_2OH (5.0 equiv)	—[e)]
5	H_2O (5%)[f)]	67
6	AcOH (20%)[f)]	5[g)]
7	CF_3CO_2H (5.0 equiv)	0[g)]
8	$2,4,6\text{-}(NO_2)_3C_6H_2OH$ (5.0 equiv)	0[g)]

a) All reactions were carried out using **2d** (0.5 mmol), CuI (1.0 mmol), a given additive, and acetonitrile (10 mL) at 40 °C for 24 h. b) Isolated yield. c) Additive was recovered almost unchanged. d) 24% of the additive was recovered. e) A complex mixture containing **1d**, **2d** and added phenol was obtained. f) Amount relative to acetonitrile. g) A mixture of trihalogenoolefines was isolated in ca. 40% (Entry 6), 10% (Entry 7) and 30% (Entry 8) yields, respectively (see the text).

tron scavenger, as well as added water did not much affect the yield of iodide **1d** (Entries 2, 5). However, the radical scavengers such as 1,1-diphenylethene and 2,6-di-*t*-butyl-4-methylphenol lowered considerably the yield of **1d** (Entries 3, 4). When a small amount of protic acid such as acetic, trifluoroacetic, or picric acid was added, the formation of iodide **1d** was almost completely suppressed and a mixture of three mixed trihaloolefins, ArBrC=CIBr, ArIC=CBr_2, and ArIC=CIBr (Ar = 4-ClC_6H_4), was obtained instead. However, hydrodehalogenation and hydrohalogenation products, ArC≡CH, ArCH=CXY, and ArCX=CHY, were not detected in the product mixture (Entries 6—8).

Competitive halogen exchange reaction has been carried out for a series of 1-bromoalkynes **2a—h,k—m** and the results are summarized in Table 6. Both electron-withdrawing and electron-donating substituents at *para* position were found to facilitate the reaction. The chlorine atom at *meta* position also worked favorably, but the same substituent at *ortho* position worked adversely (Entries 9, 10). The methyl group at *ortho* position similarly showed a negative effect, in contrast to a weak positive effect of the same group at *para* position (Entry 11). The prominent retarding effect of the *ortho* substituent groups, irrespective of their electronic nature, strongly suggests the importance of the coordination of a copper species toward the acetylenic bond.

Table 6. Competitive Iodination of 1-Bromoalkynes **2a—h,k—m** in the Presence of Excess CuI[a)]

Entry	Substituent X	k_X/k_H[b)]	$\log k_X/k_H$	Hammett σ[c)]
1	H	1.00	0.00	0.00
2	4-Me	1.08	0.04	−0.17
3	4-MeO	1.12	0.05	−0.27
4	4-Cl	1.32	0.12	0.23
5	4-Br	1.36	0.13	0.23
6	$4\text{-MeO}_2\text{C}$	1.33	0.12	0.45
7	4-CN	1.82	0.26	0.66
8	4-NO_2	2.06	0.31	0.78
9	3-Cl[d)]	1.29	0.11	0.37
10	2-Cl[d)]	0.72	−0.33	
11	2-Me	0.78	−0.24	

a) All reactions were carried out using an equimolar amount (0.25 mmol) of **2d** and a given 1-bromoalkyne in the presence of CuI (2.5 mmol) in acetonitrile (20 mL) at 24 °C, unless otherwise noted. b) Relative consumption rate of 1-bromoalkynes. c) Taken from Ref. 38. d) Competition with **2a**.

The Hammett plot for the competitive halogen exchange of 1-bromoalkynes **2a—h,l** is shown in Fig. 4. The general appearance of the plot looks V-shaped, the parent alkyne **2a** being located at the intersection of two gentle slopes. The estimated ρ value for a right-hand slope is +0.35 and that for a left-hand slope is −0.18. The V-shaped trends in Hammett correlation have previously been observed for the reactions involving the benzylic and styrenic radical species.[39)]

The effect of additives on the sulfonylation of 1-iodoalkyne **1a** with copper(II) bis(4-methylbenzenesulfinate) has also been examined; the results are summarized in Table 7. Acetic acid and DNB did not show any remarkable influence on the yield of sulfone **4a**. *trans*-Stilbene and diphenylacetylene, which are expected to trap 4-methylbenzenesulfonyl iodide if generated in situ, did not give any expected addition products. On the other hand, the addition of 1,1-diphenylethene led to the formation of a considerable amount of 2,2-diphenylvinyl 4-methylphenyl sulfone[40)] (**6**), as shown in Scheme 2.

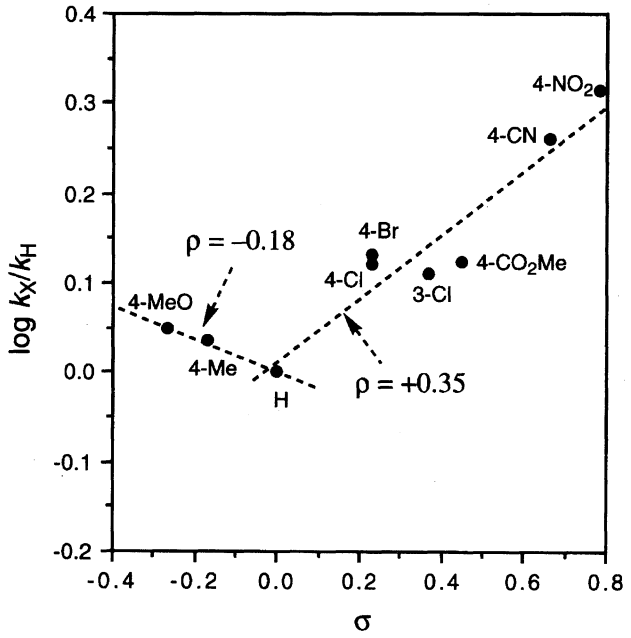
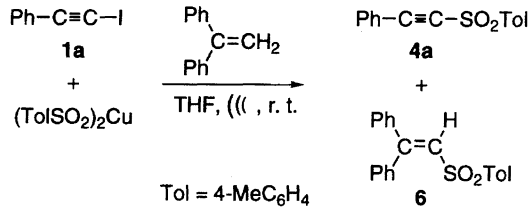


Fig. 4. Hammett plot for the iodination of 3- and 4-substituted phenylethynyl bromides **2** in acetonitrile at 24 °C.

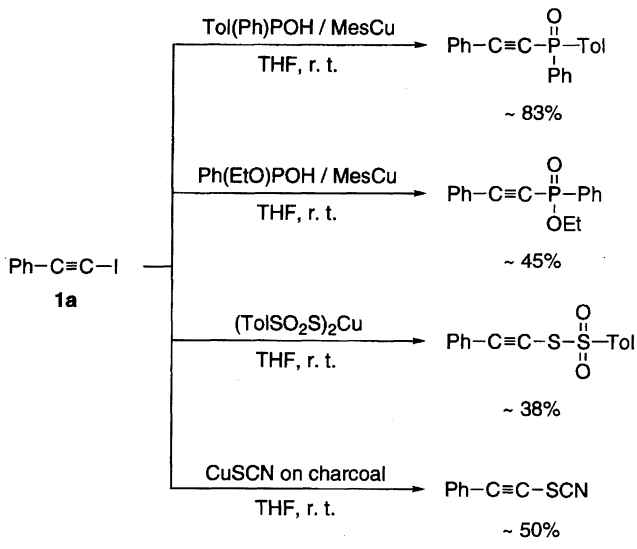
As the extension of the present work, halogen displacement of 1-haloalkynes by other heteroatom nucleophiles has been examined by using **1a** as the common substrate in the presence of a copper(I) or (II) compound. Several reactions involving some sulfur or phosphorus nucleophiles were found to lead to the expected substitution products in moderate to good yields, as illustrated in Scheme 3. However, the duplication of these reactions was often unsatisfactory, especially with regard to the yields. The reason is not clear at present.

Discussion

With respect to the non-catalyzed *sp* carbon-centered nucleophilic displacement reactions, three different mechanisms have been proposed to date, as illustrated in Scheme 4.[1,2,41)] These mechanisms are distinguished one from the other by the position where the nucleophile attaches as well as by the mode by which it attaches. In accord with these heterolytic representations, we may depict the corresponding three possible routes *a*—*c* for the present copper-assisted halogen exchange reaction between 1-bromoalkynes **2** and



Scheme 2.



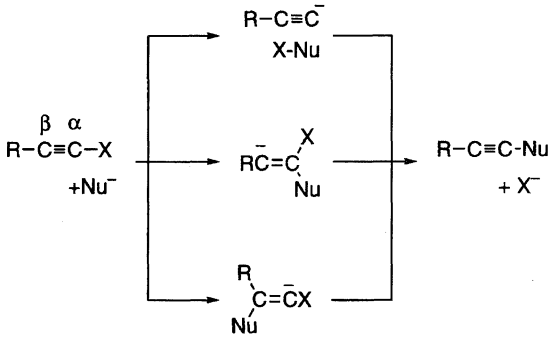
Tol = 4-MeC_6H_4; Mes = 2,4,6-$Me_3C_6H_2$

Scheme 3.

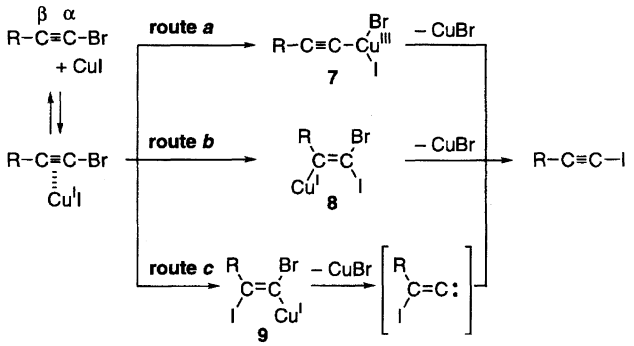
Table 7. The Effect of Additives on the Sulfonylation of 1-Iodoalkyne **1a**[a)]

Entry	Reagent[a)] (equiv)	Conditions			Product/%[b)]		
		Solvent	Method[a)]	Time/h	**4a**	**5a**	Unchanged **1a**
1	Tos_2Cu (0.67), $Ph_2C{=}CH_2$ (3.0)	THF	U	4	41[c)]	0	0
2	Tos_2Cu (0.5), *trans*-PhCH=CHPh (1.0)	THF	U	4	50	0	—[d)]
3	Tos_2Cu (0.5), PhC≡CPh (1.0)	DMF	M	4	52[e)]	0	16
4	Tos_2Cu (0.67), $1,2\text{-}(NO_2)_2C_6H_4$ (1.0)	THF	U	4	65	0	0
5	Tos_2Cu (0.67), AcOH (1.0)	THF	U	5	76	Trace	Trace

a) See footnote in Table 3. b) Isolated yield. c) $Ph_2C{=}CHSO_2Tol$ (**6**) was also obtained in 39% yield based on **1a**. d) Not determined. e) PhC≡CPh was mostly recovered unchanged (90%).



Scheme 4.



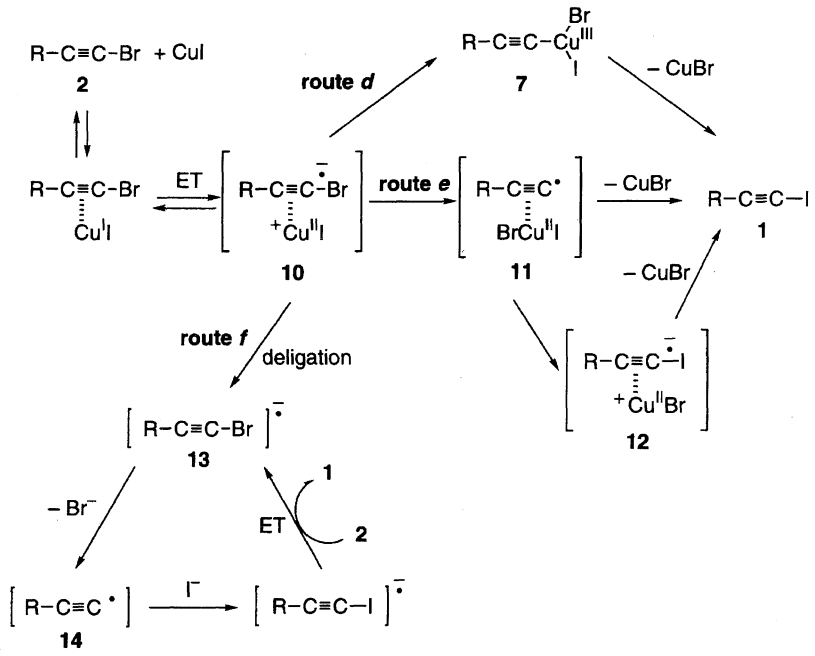
Scheme 5.

CuI (Scheme 5): (*a*) Oxidative insertion of CuI into the C–Br bond, followed by reductive elimination of 1-iodoalkyne; (*b*) *Cis*-addition of CuI toward the triple bond with iodine atom at a terminal carbon, followed by *trans*-1,2-elimination of CuBr; and (*c*) *Cis*-addition of CuI toward the triple bond in an opposite orientation, followed by α-elimination of CuBr and subsequent 1,2-migration of iodine atom in the resulting carbenoid intermediate. It would be reasonable to assume the formation of a 1 : 1 complex between **2** and CuI at initial stage, since the η^2-alkyne copper(I) complexes have long been known for their ease of formation and good stability,[42)] From the kinetic data, such mechanistic pathways that need to involve multiple molecules of CuI or 1-bromoalkyne **2** in the rate equation should be ruled out.

Furthermore, three additional mechanistic routes *d*—*f* may be worth taking into consideration. All these involve the single electron transfer from CuI to 1-bromoalkyne as the key step, where an alkyne radical anion-copper(II) complex (**10**) is assumed as the common intermediate (Scheme 6): (*d*) Oxidative insertion of CuI to C–Br bond, followed by reductive elimination of 1-iodoalkyne; (*e*) Intimate electron transfer,[43)] followed by the migration of a halogen atom from carbon to copper,[44)] and vice versa to form alkyne radical-copper(II) complexes like **11**, which collapses directly or via an intermediate **12** to 1-iodoalkyne and CuBr; and (*f*) $S_{RN}1$ type cyclic chain mechanism involving a 1-bromoalkyne radical anion (**13**) as the chain carrier.[45)]

Protic organic solvents like alcohols have frequently been used as a probe for detecting carbanion intermediates.[33)] Under our protic conditions, however, little or no hydrodehalogenation and hydrohalogenation products were detected (Table 5, Entries 5—8). If vinylcopper species like **8** and **9** are generated during the course of reaction, they should be protonated in part to afford dihalogenated olefins. This was not the case. Thus, we can exclude the routes *b* and *c*. Formation of highly oxidized copper(III) species **7** as a discrete intermediate in routes *a* and *d* is doubtful, especially under such mild conditions as employed. The radical scavengers were found to lower the yield of **1d** remarkably (Table 5, Entries 3,4). This observation suggests possible intermediacy of a free and/or coordinated radical species such as **14** and **11**. In contrast, DNB gave little effect on the product yield (Entry 2), ruling out a possible intervention of the nucleophilic radical chain route *f*. Furthermore, the route *f* is inconsistent with the linear dependence of the reaction rate on the CuI concentration.

Based on these findings and consideration, we propose that the route *e* is the most plausible answer as to the mechanistic pathway at the present stage of our study. The competitive kinetic study has revealed that both electron-withdrawing and electron-donating groups on aromatic ring facilitate the halogen-halogen exchange of **2**. Such observation may be consistent only with the route *e*, which assumes the reversible generation of **10** via ligation and electron transfer. The ligation stage is subject to the electron density of the triple bond and, therefore, would be facilitated by the electron-donating groups and retarded by the electron-withdrawing groups. In contrast, the subsequent electron transfer stage would be fa-



Scheme 6.

cilitated by the electron-withdrawing groups that stabilize the anionic center. At the stage of the C–Br bond fission, both electron-withdrawing and electron-donating groups are expected to stabilize the resulting radical species **11**, since the unpaired electron in **11** can be dissipated onto the aromatic ring as well as onto a substituent group, without regard to their electronic nature. A similar tendency has been reported in some homolytic aromatic substitution reactions.[46]

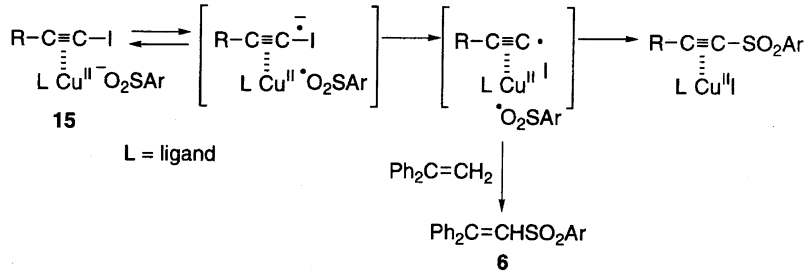
The adverse effect of *ortho*-substituent groups may be attributed to steric hindrance toward the ligation of the copper(I) reagent to the acetylenic linkage (Table 6, Entries 10, 11). The negative effect of heterogeneous conditions as well as too high concentration of CuI may also be attributed to the increased steric bulkiness of the copper reagent due to molecular aggregation (Table 1, Entries 5—7 and Fig. 3).

The ρ values estimated from Fig. 4 are small as compared with those reported for other nucleophilic displacement reactions of 1-haloalkynes,[2] where the nucleophilic attack occurs on terminal acetylenic carbon ($\rho = 2.0$—5.1) or halogen atom ($\rho = 1.15$—2.0). Small ρ values observed, as well as the V-shaped appearance of the Hammett plot, may be taken to support the operation of a radical ion mechanism in the copper(I)-assisted displacement of 1-haloalkynes. Formation of 1,3-diynes **5a**—**c** was always observed in the iodination of electron-rich substrate **2a**—**c** (Table 2). Arylethynyl radicals are known for their electrophilic nature,[47] so the electron-donating substituents favor the deligation of intermediate **11** to form radical **14**, resulting in the formation of its dimer **5** as a side product.

The CuI-assisted one-way conversion of bromoalkynes **2** to iodoalkynes **1** and the failure of the halogen–halogen exchange for other combinations of 1-haloalkynes and copper(I) halides may need some comments. This uniqueness can be qualitatively understood on the basis of thermochemical considerations. The reduction potentials of 1-haloalkynes **1a**—**3a** are -1.68, -2.00, and -2.29 V versus SCE, respectively,[48] where the ease of electron transfer to 1-haloalkynes increases in the order **3a** < **2a** < **1a**. The dissociation energies D^0_{298} of covalent Cu(I)–X bonds are 382.8 ± 4.6 for Cu–Cl, 331 ± 25 for Cu–Br, and 197 ± 21 kJ mol^{-1} for Cu–I, respectively, which decrease in the order **3a**>**2a**>**1a**. The corresponding values for the C–X bond dissociation are 397 ± 29 for C–Cl, 280 ± 21 for C–Br, and 209 ± 21 kJ mol^{-1} for C–I, respectively,[49] which follows the order **3a**>**2a**>**1a**. Taking these results together, we may explain the favored conversion of 1-bromoalkynes **2** to 1-iodoalkynes **1** under mild conditions according to the inequality of energy balance D^0(Cu–I)+D^0(C–Br) < D^0(Cu–Br)+D^0(C–I). The conversion of **2** to 1-chloroalkyne **3** may also be feasible on thermochemical grounds, but in this case the electron transfer process in route *e* in Scheme 6 needs higher energy, thus disfavoring such conversion.

The acid-induced switchover of the reaction mode from the halogen–halogen exchange to the formation of trihaloolefins (Table 5, Entries 6—8) may be explained in terms of the dihalogenation of 1-haloalkyne by Cu(II)XY species (X, Y = Br or I), as proposed by Uemura et al.[50] Although the role of protic acid is not clear at present, it may facilitate the deligation of inorganic Cu(II) from a complex such as **10** or **11** by enhancing the acidity of reaction environments.

The sulfonylation of 1-haloalkynes is effected by copper(II) bis(arenesulfinate), in which the Cu(II) moiety possesses little reducing ability. Analogously to the halogen exchange, this reaction is not affected by added water and DNB, ruling out possible intervention of radical anion species as a discrete intermediate. The sulfinate anion is subject to single electron transfer oxidation,[51] so a possible mechanism for the sulfonylation may be depicted as shown in Scheme 7, in which the sulfinato ligand in copper(II) complex **15** is oxidized by activated alkyne to generate the sulfonyl radical, which couples



Scheme 7.

with the alkynyl radical counterpart to produce alkynyl sulfone **4**. The sulfonyl radical was successfully trapped by 1, 1-diphenylethene to give vinylsulfone **6** (Table 7, Entry 1);[40] a control experiment carried out in the absence of iodide **1a** produced little sulfone.

Nucleophilic displacement reaction at *sp*-carbon promoted by single electron transfer has been investigated by Bunnet et al. in the 1970's and later by Galli et al.[45] They obtained dehalogenated alkynes as predominant products, probably due to more severe reaction conditions and the higher reducing power of the reagents they used. For the present copper-mediated nucleophilic displacement of 1-haloalkynes, the intimate electron transfer mechanism depicted in Schemes 6 and 7 is more likely to explain the experimental results available at present, though further study is needed to substantiate this.

Experimental

All reactions were carried out under an argon atmosphere. Melting points were determined on a Yanaco micro melting point apparatus and are not corrected. Mass spectra (EI) were determined at 70 eV on a Shimadzu GCMS-QP2000A mass spectrometer. IR spectra were measured in a liquid film on NaCl plate or in a KBr pellet, using a Shimadzu FTIR-8100 infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Gemini 200 MHz NMR spectrometer, using tetramethylsilane as an internal standard. GC analyses were carried out using a Shimadzu GC-14A gas chromatograph equipped with a J&W Scientific DB-5 capillary column (ϕ 0.25 mm × 30 m). Aiwa Rika Kogyo AU-10C (60 W) apparatus was employed for sonication. Elemental analyses were carried out at Microanalytical Laboratory, Institute for Chemical Research, Kyoto University.

Materials. THF was distilled from sodium benzophenone ketyl before use. High purity water was purchased from Wako Pure Chemicals Industries, Ltd. All other solvents were distilled and stored over an appropriate drying agent. 1-Iodoalkynes (**1**),[9,52] 1-bromoalkynes (**2**),[3—5,8] and phenylethynyl chloride (**3a**)[53] were prepared according to the literature procedures. Commercial copper(I) halides were purified as reported.[54] Arenesulfinic acids were prepared by reducing the corresponding arenesulfonyl chlorides with aqueous sodium hydrogensulfite.[55] 1,1-Diphenylethene was carefully distilled before use. All other reagents were purchased from Wako Pure Chemicals Industries, Ltd., Nacalai Tesque, Inc., or Tokyo Kasei Kogyo Co., Ltd. and used without further purification.

CuI-Assisted Conversion of 1-Bromoalkynes 2 to 1-Iodoalkynes 1. General Procedure. A mixture of 1-bromoalkyne **2** (0.50 mmol), CuI (0.190 g, 1.0 mmol), and acetonitrile (10 mL) was stirred at 40 °C for 24 h and then diluted with water (30 mL). The organic phase was extracted with ethyl acetate (20 mL×3) and the combined extracts were washed successively with water and brine, dried over anhydrous sodium sulfate, and concentrated on a rotatory evaporator under reduced pressure. The residue was chromatographed on silica gel using hexane or hexane/ethyl acetate as the eluent.

Phenylethynyl Bromide (2a): Colorless oil;[41,56,57] mass *m/z* 182, 180 (M^+); IR (neat) 2203, 1485, 1443, 754, 689 cm^{-1}; ^{1}H NMR δ = 7.27—7.36 (3H, m), 7.42—7.48 (2H, m); ^{13}C NMR δ = 49.7, 80.0, 122.7, 128.3, 128.7, 132.0.

(4-Methylphenyl)ethynyl Bromide (2b): Colorless oil;[4,41,56,57] mass *m/z* 196, 194 (M^+); IR (neat) 2201 (weak), 1510, 814 cm^{-1}; ^{1}H NMR δ = 2.35 (3H, s), 7.11 (2H, d, *J* = 8.1 Hz), 7.33 (2H, d, *J* = 8.1 Hz); ^{13}C NMR δ = 21.5, 48.7, 80.2, 119.7, 129.1, 131.9, 138.9.

(4-Methoxyphenyl)ethynyl Bromide (2c): Colorless crystals; mp 38—40 °C (lit,[4] 39—41 °C); mass *m/z* 212, 210 (M^+); IR (KBr) 2197 (weak), 1605, 1509, 1289, 1248, 1171, 1026, 826 cm^{-1}; ^{1}H NMR δ = 3.80 (3H, s), 6.82 (2H, d, *J* = 9.0 Hz), 7.38 (2H, d, *J* = 9.0 Hz); ^{13}C NMR δ = 47.8, 55.3, 80.0, 114.0, 133.4, 159.9.

(4-Chlorophenyl)ethynyl Bromide (2d): Colorless plates; mp 90—91 °C (lit,[4] 88—90 °C); mass *m/z* 218, 216, 214 (M^+); IR (KBr) 2195 (weak), 1489, 1086, 1015, 822, 515 cm^{-1}; ^{1}H NMR δ = 7.28 (2H, d, *J* = 8.7 Hz), 7.38 (2H, d, *J* = 8.7 Hz); ^{13}C NMR δ = 51.0, 79.0, 121.2, 128.7, 133.2, 134.8.

(4-Bromophenyl)ethynyl Bromide (2e): Colorless plates; mp 97—99 °C (decomp) (lit,[4] 96—97 °C); mass *m/z* 262, 260, 258 (M^+); IR (KBr) 2197 (weak), 1483, 1069, 1011, 816, 515 cm^{-1}; ^{1}H NMR δ = 7.30 (2H, d, *J* = 8.4 Hz), 7.45 (2H, d, *J* = 8.4 Hz).

(4-Methoxycarbonylphenyl)ethynyl Bromide (2f): Colorless plates; mp 110—111 °C; mass *m/z* 240, 238 (M^+); IR (KBr) 2197, 1711, 1437, 1281, 1107, 768 cm^{-1}; ^{1}H NMR δ = 3.92 (3H, s), 7.51 (2H, d, *J* = 8.6 Hz), 7.98 (2H, d, *J* = 8.6 Hz). Found: C, 50.40; H, 2.91%. Calcd for $C_{10}H_7BrO_2$: C, 50.24; H, 2.95%.

(4-Cyanophenyl)ethynyl Bromide (2g): Colorless crystals; mp 151—152 °C (decomp) (lit,[4] 150—151 (decomp) °C); mass *m/z* 207, 205 (M^+); IR (KBr) 2230, 2195, 1601, 1497, 1406, 837, 552 cm^{-1}; ^{1}H NMR δ = 7.53 (2H, d, *J* = 8.6 Hz), 7.61 (2H, d, *J* = 8.6 Hz); ^{13}C NMR δ = 55.4, 78.6, 112.2, 118.3, 127.6, 132.1, 132.6.

(4-Nitrophenyl)ethynyl Bromide (2h): Colorless needles; mp 175—177 °C (decomp) (lit,[4] 180—182 (decomp) °C); mass *m/z* 227, 225 (M^+); IR (KBr) 2195, 1509, 1345, 855, 749, 687 cm^{-1}; ^{1}H NMR δ = 7.59 (2H, d, *J* = 8.8 Hz), 8.19 (2H, d, *J* = 8.8 Hz); ^{13}C NMR δ = 56.3, 78.4, 123.6, 129.5, 132.8, 147.4.

1-Bromo-1-octyne (2i): Colorless oil;[8] mass *m/z* 161, 159 ($M^+ - C_2H_5$); IR (neat) 2872, 2218 (weak), 1458, 1431, 1379, 1327, 725 cm^{-1}; ^{1}H NMR δ = 0.86—0.93 (3H, m), 1.2—1.6 (8H, m), 2.20 (2H, t, *J* = 6.9 Hz).

Phenylethynyl Iodide (1a): Colorless oil;[58,59] mass *m/z* 228 (M^+); IR (neat) 2170 (weak), 1489, 1443, 754, 689 cm^{-1}; ^{1}H NMR δ = 7.29—7.33 (3H, m), 7.41—7.47 (2H, m).

(4-Methylphenyl)ethynyl Iodide (1b): Colorless crystals; mp 37—38 °C (lit,[57] 39 °C); mass *m/z* 242 (M^+); IR (neat) 2164 (weak), 1509, 816 cm^{-1}; ^1H NMR δ = 2.35 (3H, s), 7.11 (2H, d, J = 8.1 Hz), 7.33 (2H, d, J = 8.1 Hz).

(4-Methoxyphenyl)ethynyl Iodide (1c): Colorless crystals; mp 62—64 °C (decomp); mass *m/z* 258 (M^+); IR (KBr) 2159 (weak), 1603, 1507, 1293, 1252, 1173, 1022, 826 cm^{-1}; ^1H NMR δ = 3.80 (3H, s), 6.83 (2H, d, J = 9.1 Hz), 7.38 (2H, d, J = 9.1 Hz). Found: C, 41.74; H, 2.61%. Calcd for C_9H_7IO: C, 41.89; H, 2.73%.

(4-Chlorophenyl)ethynyl Iodide (1d): Colorless crystals; mp 86—87 °C (lit,[60] 84.7—85.0 °C); mass *m/z* 264, 262 (M^+); IR (KBr) 2163 (weak), 1485, 1080, 1013, 824, 664, 519 cm^{-1}; ^1H NMR δ = 7.28 (2H, d, J = 8.3 Hz), 7.36 (2H, d, J = 8.3 Hz).

(4-Bromophenyl)ethynyl Iodide (1e): Colorless crystals; mp 94—96 °C (decomp) (lit,[60] 93.8—94.0 °C); mass *m/z* 308, 306 (M^+); IR (KBr) 2163 (weak), 1483, 1069, 1013, 820, 517 cm^{-1}; ^1H NMR δ = 7.29 (2H, d, J = 8.6 Hz), 7.45 (2H, d, J = 8.6 Hz). Found: C, 31.45; H, 1.23%. Calcd for C_8H_4BrI: C, 31.31; H, 1.31%.

(4-Methoxycarbonylphenyl)ethynyl Iodide (1f): Colorless crystals; mp 135—137 °C (decomp); mass *m/z* 286 (M^+); IR (KBr) 2170 (weak), 1725, 1701, 1603, 1437, 1279, 1107, 768 cm^{-1}; ^1H NMR δ = 3.92 (3H, s), 7.49 (2H, d, J = 8.6 Hz), 7.99 (2H, d, J = 8.6 Hz). Found: C, 41.88; H, 2.37%. Calcd for $C_{10}H_7IO_2$: C, 41.99; H, 2.47%.

(4-Cyanophenyl)ethynyl Iodide (1g): Colorless needles; mp 169—171 °C (decomp); mass *m/z* 253 (M^+); IR (KBr) 2234, 2166, 1599, 1497, 1404, 841, 556 cm^{-1}; ^1H NMR δ = 7.50 (2H, d, J = 8.6 Hz), 7.60 (2H, d, J = 8.6 Hz). Found: C, 42.98; H, 1.47; N, 5.49%. Calcd for C_9H_4IN: C, 42.72; H, 1.59; N, 5.54%.

(4-Nitrophenyl)ethynyl Iodide (1h): Colorless crystals; mp 181—183 °C (decomp) (lit,[60] 181—182 °C); MS *m/z* 273 (M^+); IR (KBr) 2170, 1507, 1341, 853, 749, 687 cm^{-1}; ^1H NMR δ = 7.58 (2H, d, J = 9.0 Hz), 8.19 (2H, d, J = 9.0 Hz).

1-Iodo-1-octyne (1i): Colorless oil;[58] mass *m/z* 236 (M^+); IR (neat) 2188 (weak), 1456, 1429, 1379, 1325, 725 cm^{-1}; ^1H NMR δ = 0.85—0.92 (3H, m), 1.2—1.6 (8H, m), 2.35 (2H, t, J = 6.9 Hz).

(2,4,6-Trimethylphenyl)ethynyl Iodide (1j): Colorless plates; mp 89 °C (decomp) (lit,[41] 90—91 °C); mass *m/z* 270 (M^+); IR (neat) 2911, 2149, 1607, 857, 725 cm^{-1}; ^1H NMR δ = 2.27 (3H, s), 2.39 (6H, s), 6.85 (2H, s).

Phenylethynyl Chloride (3a): Colorless oil;[53] mass *m/z* 138, 136 (M^+); IR (neat) 2224, 1489, 1445, 754, 689, 656 cm^{-1}; ^1H NMR δ = 7.25—7.35 (3H, m), 7.41—7.47 (2H, m).

Preparation of Copper(II) Bis(4-methylbenzenesulfinate). A mixture of basic copper(II) carbonate (approximate composition, $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$; 12.0 g, 0.05 mol), 4-methylbenzenesulfinic acid (prepared from sodium 4-methylbenzenesulfinate and hydrochloric acid; 46.9 g, 0.30 mol), and THF (100 mL) was stirred overnight at room temperature. The insoluble material was filtered off, repeatedly washed with THF, and dried in vacuo. The resulting pale green powder was used for subsequent sulfonylation without further purification.

Preparation of Alkynyl Sulfones 4. a) From Iodoalkynes 1 and Copper(II) Bis(4-methylbenzenesulfinate). A mixture of iodoalkyne **1** (1.0 mmol), copper(II) bis(4-methylbenzenesulfinate) (0.3 g, 0.7 mmol), and THF (3 mL) was sonicated for 4 h. The mixture was diluted with THF (10 mL) and filtered through a Celite bed. The filtrate was evaporated under reduced pressure to leave a solid residue, which was chromatographed on silica gel using hexane/ethyl acetate as the eluent to give the expected alkynyl sulfone **4**.

b) From Iodoalkynes 1, Basic Copper(II) Carbonate, and Arenesulfinic Acid. The same procedure as above was followed, except that a combination of commercial basic copper(II) carbonate (0.08 g, 0.34 mmol) and arenesulfinic acid (1.34 mmol) was used in place of copper(II) bis(4-methylbenzenesulfinate).

4-Methylphenyl Phenylethynyl Sulfone (4a): Colorless needles; mp 85—86 °C (lit,[61] 82—83 °C); mass *m/z* 256 (M^+); IR (KBr) 2182, 1329, 1156, 1084, 850, 681, 552 cm^{-1}; ^1H NMR δ = 2.47 (3H, s), 7.31—7.55 (7H, m), 7.96 (2H, d, J = 8.4 Hz). Found: C, 70.26; H, 4.58%. Calcd for $C_{15}H_{12}O_2S$: C, 70.29; H, 4.72%.

(4-Methoxycarbonylphenyl)ethynyl 4-Methylphenyl Sulfone (4f): Colorless crystals; mp 146—148 °C; mass *m/z* 314 (M^+); IR (KBr) 2184, 1329, 1156, 1184, 851, 681, 552 cm^{-1}; ^1H NMR δ = 2.48 (3H, s), 3.93 (3H, s), 7.41 (2H, d, J = 8.2 Hz), 7.59 (2H, d, J = 8.6 Hz), 7.97 (2H, d, J = 8.2 Hz), 8.03 (2H, d, J = 8.6 Hz). Found: C, 64.79; H, 4.45%. Calcd for $C_{17}H_{14}O_4S$: C, 64.95; H, 4.49%.

(4-Cyanophenyl)ethynyl 4-Methylphenyl Sulfone (4g): Colorless plates; mp 143—144 °C; mass *m/z* 281 (M^+); IR (KBr) 2230, 2186, 1341, 1157, 1082, 812, 666, 590 cm^{-1}; ^1H NMR δ = 2.49 (3H, s), 7.42 (2H, d, J = 8.3 Hz), 7.60—7.70 (4H, m), 7.96 (2H, d, J = 8.3 Hz). Found: C, 68.30; H, 3.79; N, 5.08%. Calcd for $C_{16}H_{11}NO_2S$: C, 68.31; H, 3.94; N, 4.98%.

4-Methylphenyl (4-Nitrophenyl)ethynyl Sulfone (4h): Colorless crystals; mp 166—167 °C (decomp); mass *m/z* 301 (M^+); IR (KBr) 2186, 1539, 1348, 1157, 1086, 868, 711, 540 cm^{-1}; ^1H NMR δ = 2.49 (3H, s), 7.43 (2H, d, J = 8.4 Hz), 7.70 (2H, d, J = 8.9 Hz), 7.97 (2H, d, J = 8.4 Hz), 8.24 (2H, d, J = 8.9 Hz). Found: C, 59.95; H, 3.70; N, 4.60%. Calcd for $C_{15}H_{11}NO_4S$: C, 59.79; H, 3.68; N, 4.65%.

4-Methylphenyl 1-Octynyl Sulfone (4i): Colorless oil;[62] mass *m/z* 264 (M^+); IR (neat) 2930, 2201, 1597, 1331, 1161, 1090, 679, 547 cm^{-1}; ^1H NMR δ = 0.82—0.90 (3H, m), 1.2—1.4 (6H, m), 1.5—1.6 (2H, m), 2.34 (2H, t, J = 7.0 Hz), 2.46 (3H, s), 7.36 (2H, d, J = 8.3 Hz), 7.88 (2H, d, J = 8.3 Hz).

4-Methylphenyl (2,4,6-Trimethylphenyl)ethynyl Sulfone (4j): Colorless crystals; mp 94—95 °C; mass *m/z* 298 (M^+); IR (KBr) 2163, 1331, 1159, 1086 cm^{-1}; ^1H NMR δ = 2.28 (3H, s), 2.31 (6H, s), 2.47 (3H, s), 6.85 (2H, s), 7.38 (2H, d, J = 8.3 Hz), 7.96 (2H, d, J = 8.3 Hz). Found: C, 72.50; H, 6.09%. Calcd for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08%.

Phenyl Phenylethynyl Sulfone (4n): Colorless crystals; mp 70—72 °C (lit,[61] 70—72 °C); mass *m/z* 242 (M^+); IR (KBr) 2186, 1325, 1159, 1086, 855, 727, 687, 658, 575, 542 cm^{-1}; ^1H NMR δ = 7.33—7.71 (8H, m), 8.09 (2H, d, J = 8.3 Hz).

1-Naphtyl Phenylethynyl Sulfone (4o): Colorless crystals; mp 141—143 °C (decomp); mass *m/z* 292 (M^+); IR (KBr) 2180, 1329, 1165, 1132, 851, 768, 735, 579, 498 cm^{-1}; ^1H NMR δ = 7.20—7.81 (8H, m), 7.99 (1H, d, J = 7.7 Hz), 8.17 (1H, d, J = 8.4 Hz), 8.43 (1H, d, J = 7.3 Hz), 8.88 (1H, d, J = 8.7 Hz). Found: C, 74.25; H, 4.06%. Calcd for $C_{18}H_{12}O_2S$: C, 73.95; H, 4.14%.

4-Acetamidophenyl Phenylethynyl Sulfone (4p): Colorless crystals; mp 136—137 °C; mass *m/z* 299 (M^+); IR (KBr) 3360, 2180, 1690, 1530, 1325, 1154, 1086, 850 cm^{-1}; ^1H NMR δ = 2.24 (3H, s), 7.32—7.55 (5H, m), 7.63 (1H, br s), 7.76 (2H, d, J = 8.9 Hz), 8.01 (2H, d, J = 8.9 Hz). Found: C, 63.68; H, 4.27; N, 4.44%. Calcd for $C_{16}H_{13}NO_3S$: C, 63.95; H, 4.34; N, 4.43%.

4-Nitrophenyl Phenylethynyl Sulfone (4q): Colorless crystals; mp 136—138 °C; mass *m/z* 287 (M^+); IR (KBr) 2184, 1532, 1345, 1159, 1086, 685, 536 cm^{-1}; ^1H NMR δ = 7.36—7.46 (2H,

m), 7.49—7.59 (3H, m), 8.29 (2H, d, $J = 9.1$ Hz), 8.46 (2H, d, $J = 9.1$ Hz). Found: C, 58.45; H, 3.03; N, 4.74%. Calcd for $C_{14}H_9NO_4S$: C, 58.53; H, 3.16; N, 4.88%.

4-Methylphenyl (4-Methylphenyl)ethynyl Sulfone (4r): Colorless needles; mp 104—106 °C; mass *m/z* 270 (M^+); IR (KBr) 2180, 1331, 1159, 1086, 824, 671, 608, 550 cm^{-1}; ^1HNMR $\delta = 2.37$ (3H, s), 2.47 (3H, s), 7.17 (2H, d, $J = 8.1$ Hz), 7.36—7.44 (4H, m), 7.96 (2H, d, $J = 8.3$ Hz). Found: C, 71.00; H, 5.17%. Calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22%.

Kinetic Measurement. All reactions were carried out in acetonitrile at 40±1 °C using a temperature-controlled oil bath. Biphenyl was used as an internal standard. During the course of up to 50% conversion, 5—7 aliquots of samples were drawn form the reaction flask at intervals and each was diluted with a 1 : 1 hexane–ethyl acetate mixture, washed twice with water to remove copper salt and acetonitrile, quickly filtered, and subjected to GC analysis.

Competitive Iodination of Bromoalkynes 2 with CuI. A pair of the given bromoalkynes **2** (each 0.25 mmol) and an internal standard (biphenyl or cyclododecane) were dissolved in acetonitrile (20 mL), CuI (2.5 mmol) was added, and the resulting mixture was stirred at 24±1 °C. More than 8 aliquots of samples were taken intermittently from the reaction flask and brought to GC analysis after the above-mentioned workup. Bromides **2a—c,e—h** and (2-methylphenyl)ethynyl bromide **2m** were competed with **2d**, and (2-chloro- and 3-chlorophenyl)ethynyl bromides **2k,l** were competed with **2a**. The relative consumption rates (k_X/k_H) were estimated from the integration ratio of the respective GC peak areas of substrate **2** and an internal standard.

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